ZnO–Al2O3 and ZnO–TiO2 Core–Shell Nanowire Dye-Sensitized Solar Cells

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We describe the construction and performance of dye-sensitized solar cells (DSCs) based on arrays of ZnO nanowires coated with thin shells of amorphous Al2O3 or anatase TiO2 by atomic layer deposition. We find that alumina shells of all thicknesses act as insulating barriers that improve cell open-circuit voltage (VOC) only at the expense of a larger decrease in short-circuit current density (JSC). However, titania shells 10−25 nm in thickness cause a dramatic increase in VOC and fill factor with little current falloff, resulting in a substantial improvement in overall conversion efficiency, up to 2.25% under 100 mW cm−2 AM 1.5 simulated sunlight. The superior performance of the ZnO–TiO2 core–shell nanowire cells is a result of a radial surface field within each nanowire that decreases the rate of recombination in these devices. In a related set of experiments, we have found that TiO2 blocking layers deposited underneath the nanowire films yield cells with reduced efficiency, in contrast to the beneficial use of blocking layers in some TiO2 nanoparticle cells. Raising the efficiency of our nanowire DSCs above 2.5% depends on achieving higher dye loadings through an increase in nanowire array surface area.

Introduction

Dye-sensitized solar cells (DSCs) are typically constructed from thick films of TiO2, SnO2, or ZnO nanoparticles that are sintered into a mesoporous network with a large internal surface area for the adsorption of light-harvesting dye molecules. Under illumination, dye excited states undergo rapid charge separation, with electrons injected into the nanocrystalline film and holes leaving the opposite side of the device by means of redox species in a liquid or solid-state electrolyte. Electron transport through the nanoparticle network occurs by trap-mediated diffusion, a slow mechanism (with electron escape times of 1−10 ms for ~10-μm-thick TiO2 films) that is nonetheless efficient for TiO2 cells that use the traditional I3−/I− redox couple in a liquid electrolyte. State-of-the-art liquid-electrolyte TiO2 DSCs show near-unity external quantum efficiency at wavelengths near the absorption maximum of the dye. Such efficient charge collection is possible despite slow electron transport because of the order-of-magnitude slower recombination of photoinduced electrons with I3− in the electrolyte. This delicate balance between transport and recombination is easily destroyed by attempts to improve cell stability or push cell efficiency above its longstanding record2−3 of 10−11% by, for example, (i) replacing the volatile liquid electrolyte and I3−/I− couple with nonvolatile5,6 or solid-state alternatives,7−9 (ii) thickening the nanocrystalline film to improve its light absorption and quantum yield at red wavelengths,10 or (iii) adopting a different nanocrystalline material in the hope of speeding up electron transport and slowing recombination.

In principle, a substantial increase in DSC efficiency is attainable with one of three fixes. The fix with the greatest potential to boost performance is to employ a new sensitizer with a higher molar extinction coefficient and broader spectral response than existing dyes. The development of new panchromatic dyes or dye cocktails that break the 10% efficiency limit is an unmet challenge and important focus of current research. A second fix, with a somewhat smaller efficiency payoff, is to improve cell open-circuit voltage (VOC), which is determined by the energy difference between the quasi-Fermi level of electrons within the TiO2 film and the Fermi level of the redox couple. It is thermodynamically and kinetically feasible to squeeze an additional 300−400 mV from the TiO2 DSC by lowering its dark current and, more importantly, utilizing a redox couple more closely matched to the energy of the oxidized dye. All else being equal, a 300 mV increase in VOC would mean a 35% improvement in device efficiency (to ~14%).

The third way to boost DSC efficiency is to maximize red light conversion by increasing the diffusion length of electrons within the nanocrystalline oxide, Ld, relative to the thickness of the oxide film, d, such that Ld/d ≫ 1 and d > α−1, where α is the wavelength-dependent absorption coefficient of the sensitized film. Cell photocurrent is maximized if Ld ≫ d > α−1 for all absorbed wavelengths because light harvesting and carrier collection are then very efficient. Presently the best TiO2 cells feature Ld/d ≤ 2 with d = 10−15 μm and d < α−1 for wavelengths greater than 650 nm.15−18 This is sufficient to achieve high external quantum yields across most of the visible spectrum, but Ld/d is too small to permit thickening the oxide film to maximize red light absorption. The low Ld/d ratio of nanocrystalline TiO2 has motivated recent efforts to reduce d (while maintaining d > α−1) by using sensitizers with larger absorption coefficients10 or nanocrystalline films with very high specific surface areas.19 Attempts to increase Ld itself, which depends on the electron diffusivity D, and the electron lifetime τe according to Ld = (Dτe)1/2, have focused on slowing interfacial recombination (i.e., increasing τe) by adding surface

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coatings to the nanocrystalline film or speeding up electron transport (i.e., increasing \(D_n\)) by replacing TiO\(_2\) with a different oxide in which electrons move faster. The surface treatment strategy shows promise and is the main subject of this paper. The latter approach fails, apparently because electron diffusion within the nanocrystalline film is the rate-limiting step in the recombination process, making \(D_n \propto \tau_n^{-1}\) and negating any positive impact of faster electron motion.\(^{1,20}\) Faster transport can be expected to improve DSC efficiency only when it does not trigger proportionally faster recombination.

We recently introduced a new DSC architecture based on an array of single-crystalline ZnO nanowires that should show a weaker link between diffusion and recombination and enable the faster transport that occurs in nanowires to yield a larger \(L_n\) and improved quantum yield for red light.\(^{21}\) Better electron transport in these nanowire films is a product of their excellent crystallinity and a radial electric field within each nanowire that assists carrier collection by repelling photoinjected electrons from the surrounding electrolyte. In this picture, upward band bending at the surface of each nanowire reduces the surface recombination velocity of the majority-carrier electrons regardless of the speed at which the electrons move. Recombination may remain diffusion limited, but the rate at which electrons sample the oxide surface is determined by the magnitude of the surface field rather than the diffusion constant for electrons in the wire cores. Diffusion lengths substantially larger than those of nanocrystalline films are therefore possible. Attaining a superior short-circuit current density \((J_{SC})\) with a nanowire cell of large \(L_n\) depends on fabricating single-crystalline nanowire arrays with surface areas at least as large as typical nanocrystalline films, which is a significant challenge.

Several DSCs incorporating one-dimensional nanostructures have been reported by other groups. Of these, it is unclear whether cells based on sintered TiO\(_2\) nanorod and nanotube powders\(^{22-24}\) or nanocrystalline TiO\(_2\) nanotube arrays\(^{25}\) offer any advantage in terms of their transport physics vis-à-vis the standard nanocrystalline films, since they all consist of polycrystalline percolation networks. DSCs based on branched wirelike ZnO\(^{26}\) may share the transport features of our nanowire films, but no systematic or comparative work investigating electron collection by these structures has been published.

Here we show that carrier recombination in ZnO nanowire dye-sensitized cells can be suppressed and the conversion efficiency enhanced by coating the nanowires in a conformal metal oxide shell made by atomic layer deposition (ALD). Over the past five years, many studies have described the effects of overcoating nanocrystalline TiO\(_2\) or SnO\(_2\) films in thin layers (1–30 Å) of insulating or semiconducting oxides, including NbO\(_2\), Al\(_2\)O\(_3\), MgO, SrTiO\(_3\), SiO\(_2\), Y\(_2\)O\(_3\), ZnO, SnO\(_2\), and TiO\(_2\).\(^{27-32}\) In principle, an oxide shell can suppress recombination by (i) introducing an energy barrier that increases the physical separation between photoinjected electrons and the oxidized redox species in the electrolyte, (ii) forming a tunneling barrier that corrals electrons within the conducting cores of the nanoparticle film, or (iii) passivating recombination centers on the oxide surface. A lower rate of recombination appears as a smaller dark current \((J_{dark})\), which can increase the open-circuit voltage (and fill factor) of a DSC according to the general expression \(V_{OC} = nV_{th}\ln(J_{SC}/J_{dark}) + 1\), where \(n\) is the diode ideality factor and \(V_{th}\) is the thermal voltage. Whether \(J_{SC}\) and cell efficiency also improve depends on the extent to which the electron injection and collection yields are hurt by the oxide shell. In addition to suppressing recombination, a shell can raise cell \(V_{OC}\) directly if it has a more negative conduction band edge than the core oxide or if it creates a dipole at the core–shell interface that shifts the band edge of the core upward in energy.\(^{30}\) Applying the core–shell concept to a nanowire photoelectrode provides a means to increase \(\tau_n\) and \(L_n\) by augmenting the radial surface field that reflects electrons from the nanowire–electrolyte interface.

### Experimental Methods

#### Nanowire Array Fabrication

The ZnO nanowires were grown in aqueous solution, using a two-step synthesis described elsewhere.\(^{21}\) Conductive glass substrates (F:SnO\(_2\), 8 Ω/□, Hartford Glass Co.) were ultrasonically cleaned first in ethanol/acetone and then in 1 M HCl, rinsed in ethanol, and dried under a stream of nitrogen, then coated in several monolayers of ZnO nanoparticles, 3–4 nm in diameter, by dip-coating in a concentrated ethanol solution and rinsing with clean ethanol. Nanowires were grown from these seeds by immersing substrates (up to a dozen at a time) in an aqueous solution containing 25 mM zinc nitrate hydrate, 25 mM hexamethylenetetramine, and 5–7 mM polyethyleneimine (branched, low molecular weight, Aldrich) at 92 °C for 24 h. A homemade continuous-flow reactor was used to achieve a constant nanowire growth rate during the reaction period (solution turnover time ~2.5 h). After growth, the substrates were rinsed with water and baked at 400 °C in air for 30 min to remove any residual organics. This procedure resulted in arrays of nanowires with lengths and diameters of 15 ± 2 μm and 150 ± 30 nm, respectively.

Shells of Al\(_2\)O\(_3\) or TiO\(_2\) were grown on the nanowire films in a homemade traveling-wave atomic layer deposition (ALD) system with a process pressure of 100–500 mTorr. Al\(_2\)O\(_3\) was deposited from trimethylaluminum (97%, Aldrich) and distilled water at 210 °C, using 1 s precursor pulses and a purge time of 12 s. TiO\(_2\) was deposited from TiCl\(_4\) (99.999%, Aldrich) and water at 300 °C, using a similar sequence. The average growth rate was 1.1 Å per cycle and 0.49 Å per cycle for Al\(_2\)O\(_3\) and TiO\(_2\), respectively. To expose an area for electrical contact, part of each nanowire film was removed by rubbing the substrate surface clean with a swab soaked in 1 M HCl. The arrays were then rinsed thoroughly in water and blown dry in nitrogen.

#### Cell Fabrication and Testing

Each sample was heated to 400 °C in air for 30 min and immersed while still warm in a 0.5 mM solution of N719 dye (cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) bistetraethylammonium) in acetonitrile/acet-butyl alcohol (1:1 v/v) for 1, 8, or 12 h, depending on the experiment (see below). Sensitized films were rinsed with ethanol, blown dry, and sandwiched together and bonded to thermally plated zinc counter electrodes separated by hot melt spacers (40 μm thick, Bynel, Dupont). The internal space of each cell was filled with a liquid electrolyte (0.5 M LiI, 50 mM I\(_2\), 0.5 M 4-tertbutilpyridine in 3-methoxypropionitrile (Fluka)) by capillary action. Cells were immediately tested under AM 1.5 G simulated sunlight (300 W Model 91160, Oriel). Cells were illuminated through a black aperture 0.3 cm\(^2\) in area.

#### Materials Characterization

All transmission electron microscopy (TEM) analysis was performed on a Philips CM200/FEI TEM operating at 200 kV. X-ray diffraction data were obtained on a Bruker D-8 GADDS diffractometer (Co Kα). Photoluminescence measurements were acquired with a continuous wave HeCd laser operating at 325 nm, fiber-coupled to a spectrometer and LN\(_2\)-cooled CCD detector. X-ray photoelectron spectra were recorded with a 15 kV, 40 W PHI 5400 ESCA/XPS, using an aluminum source.
The dye loading of each tested cell was determined by desorbing the dye from a second, identically prepared nanowire film in 0.01 M aqueous NaOH and measuring its absorption spectrum. Absorbance values were converted into a roughness factor (RF) for each cell, defined as the dye-coated surface area of the nanowire film divided by the projected area of the film.

Results and Discussion

ZnO–Al2O3 Core–Shell Nanowire DSCs. Amorphous alumina shells were grown on ZnO nanowire arrays by ALD, using trimethylaluminum and water at 210 °C. ALD is a stepwise chemical vapor deposition process that yields dense, smooth, and conformal Al2O3 coatings with monolayer control over the film thickness. Recently Al2O3 ALD was used to make various core−shell nanowires33 and, by etching away the nanowire cores, Al2O3 nanotubes.34 We used transmission electron microscopy (TEM) to characterize our ZnO–Al2O3 core−shell wires, choosing for ease of analysis a sample with thick shells (5.5 nm, representing 50 ALD cycles). Low-magnification TEM imaging and electron diffraction of single core−shells (Figure 1a,b) show that the alumina coating is continuous, smooth, and amorphous. Energy dispersive spectroscopy (EDS) elemental line profiles acquired across the wires (Figure 1c) are consistent with a hexagonal prismatic core−shell structure of ZnO and Al2O3. Finally, lattice-resolved images (Figure 1d) indicate that the core−shell interface is atomically abrupt and that the ZnO wires grow, as expected, along the [0001] wurtzite direction. Solar cells built from these thick-shelled arrays showed a very high series resistance but were not completely insulating (JSC < 5 μA cm−2, VOC < 0.3 V, and efficiency < 0.001% under one sun conditions).

Solar cells were constructed from ZnO−Al2O3 core−shell wire arrays with shell thicknesses up to 22 Å. Figure 2a shows J−V curves of a batch of cells made from nanowire arrays synthesized in the same growth bath. The dye loading of these cells was equalized to within 10% by sensitizing the uncoated array for 1 h and the Al2O3−coated arrays for 8 h, yielding a common roughness factor of 130 (as measured by dye desorption). The major trends in the data are a small increase in VOC and a larger decrease in JSC with increasing shell thickness. VOC plateaus and then falls for thick shells. The fill factor shows little change in this range of shell thickness. Overall, the Al2O3 shells decrease the power conversion efficiency of our nanowire DSCs. Figure 2b compares the full-scale photocurrent and dark current of each cell. As expected, alumina shells of increasing thickness progressively suppress current at all biases, especially the dark cathodic recombination current (here, the current at positive bias) and the photocurrent. This is consistent with alumina acting as a tunnel barrier that improves VOC by impeding recombination when it is very thin but blocks electron injection as it becomes thicker. The exponential decrease of the recombination current with Al2O3.
thickness supports this interpretation (see the inset in Figure 2b). The $V_{OC}$ of these core–shell cells remains higher than the $V_{OC}$ of the uncoated cells as long as the steady-state photoinjected charge density is greater. Thick shells that reduce the rate of electron injection more than the rate of recombination lower the steady-state charge density in the nanowires and hurt $V_{OC}$.

Our results are consistent with several reports of increased $V_{OC}$ and decreased $J_{SC}$ for Al$_2$O$_3$-coated nanocrystalline SnO$_2$ and TiO$_2$ electrodes, but at odds with other studies that find enhanced $V_{OC}$, $J_{SC}$, and fill factor for TiO$_2$ films with sol–gel-type Al$_2$O$_3$ overlayers. Authors of one of the latter papers established that alumina shells retard the recombination dynamics of nanocrystalline TiO$_2$ by passivating surface recombination centers and slowing the rate of interfacial charge transfer. However, we note that Al$_2$O$_3$ coatings have been shown to improve the efficiency of only relatively inefficient devices (<5%) and that no core–shell cell has yet outperformed the best TiO$_2$ cells made by Grätzel et al. In any case, these unpromising results discouraged further study of the ZnO–Al$_2$O$_3$ core–shell nanowire cells.

**ZnO–TiO$_2$ Core–Shell Nanowire DSCs.** The same ALD apparatus was used to fabricate ZnO–TiO$_2$ core–shell nanowire arrays. Here, alternating pulses of titanium tetrachloride and water at 300 °C produced continuous and conformal coatings of TiO$_2$ on the ZnO surface (Figure 3). To characterize the ALD-made titania, planar thin films were deposited on silicon and glass substrates and probed by ellipsometry, scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–vis and photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrical measurements (Figure 4). We measured an average growth rate of 0.49 Å per ALD cycle (<0.5 monolayers per cycle), which is consistent with previously reported values. The same growth rate was measured by TEM for TiO$_2$ shells grown on ZnO nanowires. TiO$_2$ films thinner than about 5 nm were completely amorphous and very smooth (Supporting Information, Figure 1). Thicker films converted to polycrystalline anatase throughout their thickness and were rougher, in agreement with previous observations. XPS surface analysis revealed trace chlorine present in some of the as-grown films. However, neither chlorine nor other impurities (except adventitious carbon) were found by XPS in films baked in air at 400 °C. These TiO$_2$ films proved too resistive ($\approx 10^4$ Ω·cm) for accurate Hall measurements with our equipment. Four-point measurements on 50-nm-thick films grown on glass and baked in air at 400 °C for 30 min gave a dark, room temperature resistivity of $\approx 10^3$ Ω·cm (with ohmic Al or Cu contacts). A two-point through-plane resistivity of $\approx 10^3$ Ω·cm was estimated by using films grown on ultraflat indium tin oxide substrates. This type of anisotropic conductivity is typical of thin films in which in-plane conduction requires carriers to cross many grain boundaries while through-plane conduction involves transport across a single crystallite, or several at most. It implies that photoinjected electrons in the ZnO–TiO$_2$ core–shell nanowire cells will tend to travel across the thin TiO$_2$ shells and into the more conductive ZnO cores.
(which have a resistivity of \(1 \Omega \cdot \text{cm}\)\(^{-1}\)); in other words, the most conductive pathway in these cells is approximately the pathway of least TiO\(_2\). A cross-sectional image of a typical core–shell array on an FTO substrate is shown in Figure 5.

We compare ZnO–TiO\(_2\) core–shell nanowire cells prepared with saturated dye loadings for maximum device efficiency. Figure 6 presents \(J–V\) data from a batch of core–shell arrays coated in different thicknesses of TiO\(_2\) and sensitized in dye for 12 h. Two control cells are included in the plots: an uncoated ZnO cell sensitized for 1 h and an uncoated ZnO cell sensitized for 12 h. The optimal sensitization time for our ZnO nanowires was 1 h, which was sufficient to achieve a high dye loading without building up Zn–dye multilayers that form from the slow etching of ZnO by the acidic N719 dye\(^{44}\). We hereafter refer to uncoated ZnO nanowire cells sensitized for 1 h as standard cells. The longer sensitization time for the TiO\(_2\)-coated cells reflects the slower rate of dye adsorption on the more acidic TiO\(_2\) surface. Twelve hours was adequate to saturate the dye loading of the core–shell arrays.

The addition of TiO\(_2\) shells to ZnO wire cells resulted in considerable improvement in both \(V_{OC}\) and fill factor (Figure 6a). For shells thicker than 10 nm, \(V_{OC}\) increased by about 250 mV to 0.78–0.82 and the fill factor jumped to 0.58–0.6, a 60% improvement. The trend in \(J_{SC}\) was more complex. The current first fell by a factor of 2–3 with the addition of ultrathin shells (0.5 nm – 5 nm) and then slowly recovered with increasing shell thickness to near the value of the standard cell. Overall, cell efficiency more than doubled in response to TiO\(_2\) shells 10–35 nm thick, jumping from 0.85% to 1.7–2.1%. The full-scale semilogarithmic plots in Figure 6b show that the dark current of the cells decreased with increasing shell thickness, which suggests that the improvement in \(V_{OC}\) and fill factor

Figure 4. Characterization of ALD TiO\(_2\) thin films. (a) Dependence of film thickness on the number of ALD cycles for films deposited at 240 and 300 °C on silicon substrates and 300 °C on ZnO nanowires. The linear fit is 0.49 Å per cycle. The thickness of samples on silicon was measured by ellipsometry, while TEM was used for shells grown on ZnO nanowires after dissolving the ZnO in 1 M aqueous HCl. (b) X-ray diffraction pattern of a TiO\(_2\) film deposited on silicon at 240 °C. All films thicker than \(\sim 5\) nm index to polycrystalline anatase, independent of growth substrate (Si, FTO, glass). (c) Extinction and transmission spectra of anatase films grown on glass at 240 and 300 °C. The inset is a photoluminescence spectrum of a film grown on silicon at 300 °C. The small peak at 388 nm is an instrument artifact. (d) XPS spectrum (Al Kα) of a film grown on silicon at 300 °C. The insets show details of the Ti 2p and Cl 2p regions. Chlorine was detected in a minority of samples; otherwise only titanium, oxygen, and adventitious carbon were found.

Figure 5. Cross-sectional SEM image of a core–shell nanowire array on FTO. Dozens of ZnO cores are visible in this damaged part of the array. Scale bar, 1 μm.
results from a suppression of recombination by the TiO$_2$ layers. A progressive suppression of the dark recombination (here, the current at positive bias, where electrons flow from the nanowires into the electrolyte) is apparent in Figure 6c. We developed a data set based on 20 devices to better quantify the performance trends of the core–shell nanowire cells. Figure 7 displays the dependence of cell fill factor, $V_{OC}$, dark current, $J_{SC}$, and efficiency on the thickness of the TiO$_2$ shell. The fill factor first falls for the thinnest shells (0.5 nm) and then immediately jumps to 0.55–0.6. This increase is driven in part by a 3-fold to 8-fold improvement in the shunt resistance, $R_{sh} (dV/dI)|_{V=0}$ (see Figure 6a). $V_{OC}$ increases even for the thinnest shells, peaks at $0.85 \text{ V}$ at a TiO$_2$ thickness of 10–15 nm, and seems to fall slightly for the thickest shells. Meanwhile, the dark anodic exchange current (the current at negative bias) and cathodic recombination current decrease by a factor of 100 and 50, respectively, before the latter increases slightly at thick TiO$_2$ to a value $\approx 20$ times smaller than that of the standard cells. A plot of the dark currents against $V_{OC}$ (Figure 8) reveals a strong inverse logarithmic relationship, $V_{OC} \propto \ln(1/J_{dark})$, as
expected for photovoltaic and photoelectrochemical cells. Linear fits to the data in Figure 8 give slopes that correspond to 144 mV/decade for the exchange current and 195 mV/decade for the recombination current. The latter value translates to a diode ideality factor $n = 3.25$, which agrees well with $n = 3.2$ as determined from fits of the illuminated current under forward bias. Overall, it is clear from these data that the TiO$_2$ shells improve $V_{OC}$ and fill factor by lowering the rate of electron–hole recombination across the oxide–electrolyte interface. A determination of precisely how the TiO$_2$ shells suppress recombination can be made only in concert with understanding the trend in $J_{SC}$, which we turn to next.

The dependence of $J_{SC}$ on shell thickness is presented in Figure 7c. The current falls dramatically upon addition of the thinnest TiO$_2$ shells, then bottoms out, steadily recovers, peaks at 15–25 nm, and finally falls off somewhat for the thickest shells. Cell efficiency tracks this trend in $J_{SC}$ quite closely. In DSCs, $J_{SC}$ is a product of the efficiencies of light harvesting, electron injection, and charge collection. The light harvesting efficiency depends directly on the dye loading, which is not constant in this data set but varies systematically with TiO$_2$ thickness. The general trend in the dye loading of these cells is a 2-fold spike for the thinnest shells followed by a gradual decrease in dye loading to about the same value as the standard cells, which themselves have the least amount of dye (see Figure 6a, in which dye loading is quantified by the roughness factor, RF). At least four factors combine to establish this trend. The initial spike in dye loading can be explained by the longer sensitization time for the core–shell cells plus incomplete coverage of ZnO by the thinnest TiO$_2$ shells (0.5 nm represents approximately two titania monolayers, which undoubtedly leaves some ZnO exposed to the acidic dye solution). The gradual decrease in dye loading with increasing TiO$_2$ thickness results in large part from the amorphous-to-anatase phase transition that begins at a shell thickness of 4–6 nm, since the amorphous surface has a greater specific dye loading.$^{45}$ In addition, the thickest shells lower the surface area available for dye adsorption by infilling some of the pore space in the bottom third of the nanowire films. The fact that the core–shell cells have more dye and thus a higher light harvesting efficiency than the standard cells means that the valley-to-peak trend in $J_{SC}$ seen in Figure 7c is caused by changes in electron injection and collection rather than light absorption.

To account for differences in dye loading, we plot the ratio of $J_{SC}$ to dye loading as a function of shell thickness in Figure 9. This ratio is a measure of the current collected per unit dye. The data are normalized to the performance of the standard cells, which show a $J_{SC}$ of 4.0–4.5 mA cm$^{-2}$ at a roughness factor of 140–160. It is clear from Figure 9 and the above discussion that dye molecules in core–shell cells are less productive than dye molecules in standard nanowire cells. For example, cells with 4-nm-thick shells contain 60% more dye but produce 60% less current than standard cells. The relative productivity of adsorbed dye improves from about 50% for cells with thin shells to around 90% for cells with the thickest shells. This trend suggests that the electron injection yield and/or transport efficiency must be improving with increasing shell thickness.

We propose that the trend in $J_{SC}$ depicted in Figures 7c and 9 is primarily a result of gradual crystallization of the TiO$_2$ shells, which begins at a threshold thickness of ~5 nm and progresses for perhaps an additional 15–20 nm of shell growth. As we discuss below, both electron injection and collection should be facilitated by the better crystallinity of thicker TiO$_2$ shells. To determine the role of the amorphous-to-anatase transition, a set of core–shell cells with completely amorphous TiO$_2$ shells was fabricated and tested. Amorphous shells were grown by ALD at 120 °C. Procedures identical with those described above were used to prepare these cells except that the core–shell films were heated to 250 °C rather than 400 °C immediately before dye sensitization. Electron- and X-ray diffraction showed that shells made in this way are amorphous regardless of thickness. The performance data and dependence of $J_{SC}$ on shell thickness for the cells with amorphous shells are shown in Figure 10. Thicker shells result in poorer overall efficiency because of a falling $J_{SC}$ and fill factor and only a marginal improvement in $V_{OC}$. Of particular importance to this discussion is the trend in $J_{SC}$ in Figure 10b. In contrast to the cells with anatase shells, the cells with amorphous shells show very little recovery of $J_{SC}$ with increasing shell thickness. $J_{SC}$ falls and does not recover because (i) electron injection into an amorphous titania surface is inefficient compared with injection into a crystalline anatase surface$^{46–48}$ and (ii) the higher density
of electron traps in amorphous titania slows electron transport and shortens the electron diffusion length. Thicker amorphous shells have a larger absolute number of traps but also a greater fraction of their volume farther from recombination sites on shells have a larger absolute number of traps but also a greater of anatase and amorphous shells strongly suggests that the Figure 11. Schematic energy level diagram of a ZnO–TiO2 core—shell nanowire in cross section and in equilibrium with the surrounding electrolyte.

of band discontinuities and with a built-in potential, neglecting any difference in densities of states, of

$$\phi_{bi} \approx V_{bi} \ln \frac{N_{D}^{+}}{N_{D}}$$

where $N_{D}^{+}$ and $N_{D}$ are the donor concentrations in the heavily doped ZnO core and more lightly doped TiO2 shell, respectively. An energy barrier of 75–150 mV is reasonable based on the likely doping difference between the ZnO and TiO2. This radial field would reduce the electron concentration at the nanowire surface by a factor of $\exp(-\phi_{bi}/kT)$, or roughly 20–300 times smaller than the concentration at the center of a nanowire, which in turn would decrease the rate of recombination. A schematic band diagram of the proposed situation is given in Figure 11.

The complex trend in $J_{SC}$ is best explained by considering three regimes of shell thickness. First, shells thinner than 5 nm are amorphous and probably electronically confined (while the exciton Bohr radius of amorphous titania is apparently unknown, that for anatase is probably 0.5–2 nm). The thinnest shells also have a very high dye loading, which implies the presence of dye aggregates on the nanowires. These effects combine to cause poor electron injection, slow diffusion, and low $J_{SC}$ values. The second regime covers shells 5–20-nm thick. Here, $J_{SC}$ steadily improves because gradual crystallization of the shells results in better electron injection and fewer bulk and surface trap sites. Our data cannot distinguish between improved injection and transport, but it is sensible to expect that some combination of the two is responsible for the recovery in $J_{SC}$. Finally, cells with very thick shells show a slight falloff in $J_{SC}$ because of a reduced surface area and smaller dye loading.

We attempted to fabricate core—shell cells of higher efficiency by using nanowire arrays of larger surface area. ZnO nanowire films were grown for up to twice the normal growth time and then coated in 20-nm-thick TiO2 shells. However, this procedure failed to produce arrays of substantially higher surface area because the thicker nanowires coalesced to a greater degree upon addition of the TiO2 shells. Our best DSCs made to date show only a 10–15% improvement in $J_{SC}$ compared with the devices in Figure 6, with efficiencies of around 2.2% (Figure 12). One could minimize nanowire coalescence and attain larger film surface areas if much thinner, fully anatase shells could be grown. This is feasible by depositing the shells at higher temperatures (closer to 400 °C), but unwise considering the limitations of our current ALD system.
The Effect of Substrate-Based TiO$_2$ Layers on Nanowire and Nanoparticle Cells. Carrier recombination in DSCs can occur across both the film—electrolyte interface and the substrate—electrolyte interface. So far we have discussed modifying the film—electrolyte interface by way of oxide shells that are deposited conformally onto the nanowire arrays. In this section, we target recombination at the substrate—electrolyte interface by depositing TiO$_2$ blocking layers underneath the nanowire films. Thin, dense layers of anatase TiO$_2$ deposited on conducting glass by spray pyrolysis are routinely used in solid-state nanoparticle DSCs to prevent short circuiting between the electrolyte interface and the solid-state nanoparticle films in electrolyte cells. Here we compare ALD-made TiO$_2$ blocking layers in nanowire and nanoparticle cells to highlight the differences between the two DSC architectures and to add to this debate.

ZnO nanowire cells and two types of TiO$_2$ nanoparticle cells were prepared on bare and TiO$_2$-coated FTO substrates. A cross-sectional image of a nanowire array on TiO$_2$-coated FTO is shown in Figure 13. The nanoparticle electrodes were made by spreading a commercial paste of 10−15 nm anatase crystals (Ti–Nanoxide T, Solaronix) on the substrates with a glass rod and sintering the films in air at 450 °C for 30 min (film thickness: 8−9 μm). One group of nanoparticle electrodes was then treated with TiCl$_4$, which is the standard treatment used to improve the $J_{SC}$ of TiO$_2$ nanoparticle cells. The TiCl$_4$ treatment was performed by soaking each film in 50 mM aqueous TiCl$_4$ solution for 10 h in an airtight container at room temperature and then rinsing with water. All films were baked in air for 30 min (at 400 °C for the nanowire films and 450 °C for the nanoparticle films) immediately before dye sensitization.

Figure 14 shows the dark and photocurrent performance of the three types of DSCs for TiO$_2$ underlayer thicknesses of 0, 10, 25, and 50 nm. Each curve is the average of three nominally identical devices. The nanoparticle cells not treated with TiCl$_4$ show slight improvements in $J_{SC}$, $V_{OC}$, and fill factor with increasing layer thickness, resulting in a 25% enhancement in conversion efficiency (to 3.3%; Figure 14a), in rough agreement with previous results.$^{62}$ The addition of an underlayer suppresses the dark current of these cells at biases negative of $V_{OC}$ (Figure 14b). The 100-fold decrease in the anodic exchange current (the current at negative bias) suggests that electron transfer from the electrolyte to FTO is blocked by the TiO$_2$ layer. Likewise, the lower dark cathodic recombination current (the current at positive bias) indicates that electron transfer from FTO to $I_3^-$ is slowed by the layer (Figure 14c). Reduced rates of recombination cause the improved performance of these untreated TiO$_2$ cells.

In contrast, the TiCl$_4$-treated nanoparticle cells show a loss of $J_{SC}$ with increasing blocking layer thickness, while $V_{OC}$ and fill factor are unaffected, resulting in a 10% loss in efficiency (to 3.2%; Figure 14d). The underlayers again cause a drastic decrease in exchange current, but only a relatively small reduction in recombination current at biases negative of 0.4 V (Figure 14e,f). We attribute the smaller effect of these layers to the lower initial recombination rate of the TiCl$_4$-treated devices. The TiCl$_4$ treatment probably passivates the most active recombination sites on the exposed FTO surface, rendering additional TiO$_2$ layers ineffectual, even counterproductive. Under illumination, these blocking layers add to the series resistance and reduce the $J_{SC}$ of these cells.

Our data provide some insight into the role of the TiCl$_4$ surface treatment. We find that it improves $J_{SC}$ by ~50% but lowers the fill factor compared to identical, untreated devices (see Figure 14a,d and the Supporting Information, Figure 4). Absorption spectra of stained films and solutions of dye desorbed from these films show that the TiCl$_4$ treatment causes a slight reduction in dye loading (Supporting Information, Figure 4). Therefore, the larger $J_{SC}$ must stem from some combination of more efficient electron injection into the nanocrystalline film and more efficient electron collection by FTO. Better injection can result if the pure TiO$_2$ layer deposited from TiCl$_4$ disfavors the formation of weakly bound dye molecules and dye aggregates. At the same time, better electron collection is possible if the TiCl$_4$-derived TiO$_2$ layer reduces the probability of photoinduced electrons recombining with triiodide. This may occur by a combination of improved interparticle connectivity (neck thickening) and a lower density of recombination sites on the purer TiO$_2$ surface. We note that our findings are at odds with a recent report that attributes the larger $J_{SC}$ to an enhanced dye loading.$^{61}$ This disagreement almost certainly reflects differences in the surface properties of the nanoparticle films used in these two studies.

We now turn to the effect of the TiO$_2$ blocking layers on the ZnO nanowire cells. Here $J_{SC}$ falls by 25% upon addition of an underlayer, while $V_{OC}$ improves slightly with layer thickness.
and the fill factor first declines and then recovers, resulting overall in a 20% loss of efficiency (to 0.87%; Figure 14g). The dark exchange current drops 10-fold and the recombination current is suppressed by a factor of 2–3 at biases negative of $V_{OC}$ (Figure 14h,i). Relative to the nanoparticle cells, the dark current of the nanowire cells is much less responsive to the addition of TiO$_2$ layers because these cells feature a dense layer of ZnO that forms at the base of the nanowire film during growth.$^{21}$ The electrolyte therefore contacts not FTO but ZnO, which partially blocks the dark current. $J_{SC}$ falls despite a smaller recombination current probably as a result of the same energy barrier at the ZnO–TiO$_2$ interface that suppresses recombination in the core–shell nanowire cells.

We draw several conclusions from the experiments in this section. First, substrate-based blocking layers primarily benefit inefficient nanoparticle cells, especially those not treated with TiCl$_4$. Second, nanoparticle DSC performance is anomalously insensitive to the magnitude of the dark exchange current. Third, the TiCl$_4$ treatment improves electron injection or transport rather than light absorption, at least for the moderately efficient nanocrystalline films used here. $^{21}$ The electrolyte therefore contacts not FTO but ZnO, which partially blocks the dark current. $J_{SC}$ falls despite a smaller recombination current probably as a result of the same energy barrier at the ZnO–TiO$_2$ interface that suppresses recombination in the core–shell nanowire cells.

Conclusions

ZnO–Al$_2$O$_3$ and ZnO–TiO$_2$ core–shell nanowire dye-sensitized solar cells have been fabricated and compared to cells built from ZnO nanowires without shells. Thin Al$_2$O$_3$ shells act as tunnel barriers that reduce recombination only at the expense of a larger reduction in electron injection yield and a lower device efficiency. TiO$_2$ shells suppress recombination and markedly improve cell open-circuit voltage and fill factor. On the basis of trends in the relevant performance parameters as a function of TiO$_2$ thickness, we attribute these effects to the passivation of surface recombination sites and the buildup of a radial energy barrier that repels electrons from the nanowire surface. Meanwhile, the valley-to-peak trend in short-circuit current is consistent with the notion that the higher crystallinity of thicker shells enables more efficient electron injection and transport. Tests of cells with thick amorphous shells confirm that large currents are obtained only with crystalline TiO$_2$ shells. ZnO–TiO$_2$ core–shell cells of optimal shell thickness and nanowire surface area achieve an efficiency of 2.25% under full sunlight. Higher efficiencies require nanowire films of larger surface area. This is best achieved by synthesizing denser arrays of thinner nanowires, rather than increasing nanowire length or diameter. For example, a hexagonal lattice of core–shell nanowires with lengths of 30 $\mu$m, a core diameter of 40 nm, a
shell thickness of 5 nm, and a pitch of 70 nm would have a surface area equal to that of a typical nanocrystalline film.

Depositing a layer of anatase TiO₂ under rather than on the nanowire films reduces dark currents only slightly because these cells already feature a thin blocking layer of ZnO at their base. Adding TiO₂ underlayers to these cells decreases both their photocurrent and efficiency, probably as a consequence of the same energy barrier at the ZnO–TiO₂ interface that suppresses recombination in the core–shell nanowire cells. The response of TiO₂ nanoparticle cells to the blocking layers depends on whether the nanoparticle films are treated with TiCl₄ before dye sensitization.

There are three reasons to believe that nanowire films may be superior to nanoparticle films in DSCs. First, nanowire films are more easily filled with the nonvolatile hole conductors needed for improved device stability. Second, electron transport within single-crystalline nanowires can be much faster than transport through nanocrystalline networks. Third, surface fields within each nanowire can be used to enforce charge separation and thereby ensure that faster transport results in a longer diffusion length. Nanoparticle DSCs lack such surface fields. Here we have presented strong but indirect evidence for the existence and importance of a surface field in core–shell nanowire DSCs, and our findings should be followed up by direct measurements of electron diffusivity and lifetime with use of time-resolved methods such as intensity modulated photocurrent and photovoltage spectroscopy. Further work is also needed to ascertain the degree to which electron injection yields depend on oxide crystallinity. Application of the core–shell concept to nanowire photoelectrodes is in an early stage and much room for optimization exists.

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Supporting Information Available: XRD and TEM data of amorphous TiO₂ nanotubes and the amorphous–anatase phase transition, performance trends for cells with amorphous TiO₂ shells, characterization of TiO₂ thin films on FTO substrates, and J–V measurements showing the effect of the TiCl₄ treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(10) From desorption measurements of core–shell nanowire films with 20-nm-thick anatase or amorphous shells sensitized for 12 h, we estimate the dye loading on amorphous titania to be about twice that of anatase titania.
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(49) Xu, Y.; Schoonen, M. A. A. Am. Mineral. 2000, 85, 543.